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Oxonium Salts of Phenolphthalein

OXONIUM SALTS OF PHENOLPHTHALEIN

BY

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THESIS

FOR THE

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DEGREE OF.....Bachelor of Science in Chemistry.....

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Chemistry

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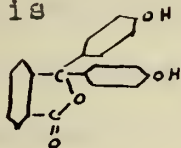
Introduction

The investigation on this particular problem was undertaken in an endeavor to find an adequate explanation of the formation of the colored compounds which are produced when phenolphthalein is treated with strongly acid substances, such as, concentrated sulfuric acid, phosphorus pentoxide, phosphorus oxychloride and anhydrous metallic salts. By isolating these compounds, their nature and that of the reactions involved might more readily be ascertained.

The problem was made difficult because of the limited amount of time in which a thorough study had to be made. The work was started and the author hopes to continue the investigation.

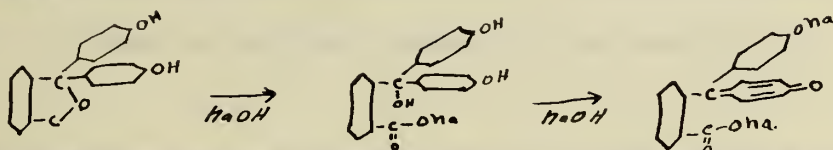
Historical

A vast amount of investigation has been made upon the compound phenolphthalein, which has the following formula, $C_{20}H_{14}O_4$, or written structurally it is



This compound can be considered to be a derivative of the tri-phenyl methane series since it has been shown that it has properties similar to compounds of this series.(1)

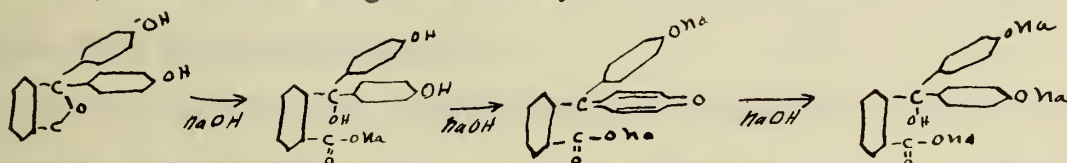
From the structure of the compound it is noticed that it possesses acid properties due to the phenolic hydroxyl groups and to the carboxyl group. Since it is a weak acid it forms salts, which are either colored or colorless. The salts which have been investigated to a very large extent are those formed in alkaline solution. In dilute alkaline solution a pink color is produced, which is decolorized by the addition of an excess of acid. With dilute NaOH the following reaction presumably takes place:



The formation of a dibasic salt of phenolphthalein with dilute NaOH was first proposed by Friedlander(2). Later Meyer and Spengler(3) proved by analysis that such a salt was formed. According to James(4) two mols of NaOH combine with one mol of phenolphthalein to produce a maximum color, which further substantiates the formation of a dibasic salt. The nature of this reaction has been the subject of much investigation. Green and

King(5), Green and Perkin(6), Acree(7), Stieglitz(8), and many others(9) have proposed various views on the subject of the salts of phenolphthalein.

In concentrated NaOH a colorless tribasic salt is produced. Kober and Marshall(10) have isolated a tribasic potassium salt, formed by the following reaction,



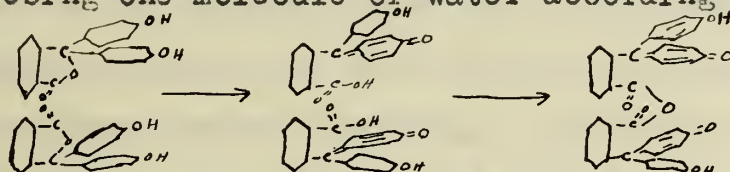
Oddo(11) has presumably prepared the mono-potassium carboxylic salt which he maintains is colored. Green and Perkin(6) maintain that a colorless mono-potassium carboxylic salt is formed.

The dibasic salt is decolorized in the presence of an excess of dilute acid. Phenolphthalein itself is also colorless in dilute acid. With strongly acid substances in the absence of water colored compounds are formed. Comparatively very little investigation has been made upon the nature of the reactions involved in producing these colored compounds. In this investigation an attempt is made to explain some of the reactions.

Experimental

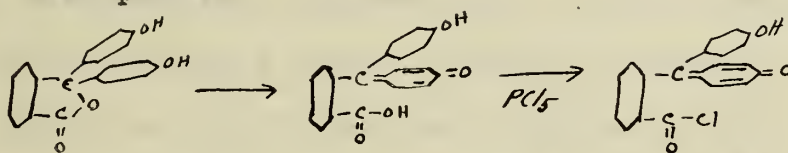
The substances used in this investigation were concentrated sulphuric acid, phosphorus pentoxide, phosphorus oxychloride and anhydrous salts, such as stannic chloride, aluminium chloride and zinc chloride. These substances produce highly colored compounds with phenolphthalein.

The nature of the substances used suggested the the possibility of an anhydride being formed, two molecules of phenolphthalein losing one molecule of water according to this equation:

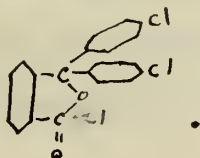


It is obvious that such a compound would be colored due to the quinoid structure. If such a compound is capable of being formed the acid chloride should also be obtained.

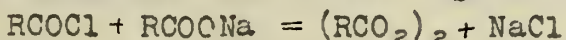
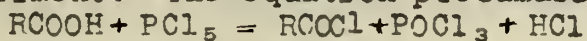
With phosphorus pentachloride the following reaction should presumably take place.



In an attempt to prepare this substance, the theoretical amount of phosphorus pentachloride and phenolphthalein were mixed in a mortar, placed in a small flask, surrounded by an oil bath and heated for two hours at 125°C. No color was obtained. According to Baeyer(12) the lactone ring is not opened and the compound formed is



Another attempt to obtain the acid chloride was made by mixing the calculated amount of sodium hydroxide, phosphorus pentachloride and phenolphthalein in a mortar and proceeding as in the previous experiment. The equation presumably being:



No colored compound was obtained. These experiments show the apparent difficulty in attacking the carboxyl group.

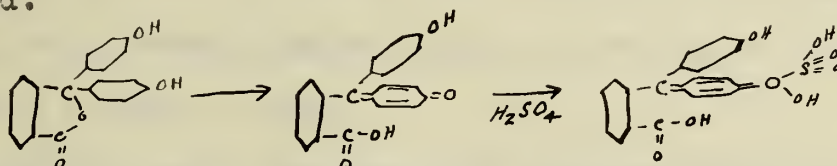
In the colored salts formed with strongly acid substances, the presence of the quinone group favors the formation of oxonium salts. Gomberg and Cone(13) have shown that oxonium formation exists in triphenyl methane compounds containing the quinone group. The work of Werner(14), Kehrman(15), and Decker and Fellenberg(16) have conclusively shown the existence of oxonium salts. The most conclusive evidence of oxonium formation has been based upon the work of K. Meyer(18) in his investigation on quinones. He found that quinones give colored compounds with anhydrous metallic salts such as stannic chloride.

Reaction with Concentrated Sulfuric Acid.

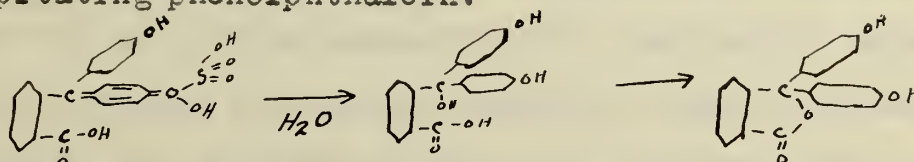
On the addition of concentrated sulfuric to phenolphthalein an orange color is produced. Baeyer(12) noted this color change, but did not isolate the compound, nor attempt to give it a definite constitution. This compound is extremely unstable, hydrolyzing on the addition of water, precipitating phenolphthalein. In the present investigation an effort was made to isolate this compound. Because of its instability isolation was impossible.

Various solvents such as dry ether, petroleum ether, absolute alcohol, amyl alcohol, methyl alcohol, gasoline, kerosene, benzene, ligroin, xylene, nitro-benzene, pyridine, chloroform, carbon bisulfide, carbon tetra chloride, etc., were used. In most cases the substance was either hydrolyzed or insoluble. A few of the solvents dissolved it, but no way was found to get rid of the excess acid which was present even when various mixtures were used.

Altho unable to isolate this compound the author believes than an oxonium salt is formed. Since it was not possible to obtain an acid chloride, the present investigation leads the author to conclude that the carboxyl group is not active in the presence of concentrated sulphuric acid. The following reaction is submitted.



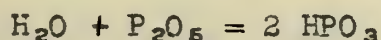
The acid first causes a rearrangement from the benzoid to the quinonoid form, then attaches itself to the oxygen of the quinone group to give the oxonium salt. The presence of an excess of acid does not alter the color. The addition of water immediately destroys the color presumably by hydrolysis, liberating the acid and precipitating phenolphthalein.



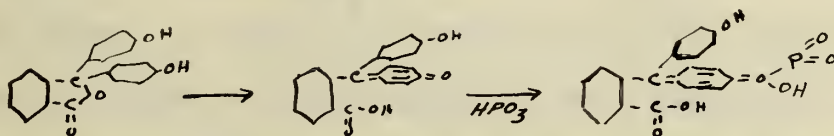
The compound first goes to the carbinol form, then immediately loses water to give the lactone.

Reaction with phosphorus pentoxide.

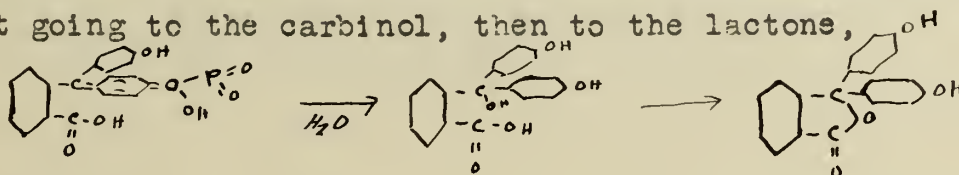
Phosphorus pentoxide has strongly acid properties, so it was studied in the same manner as concentrated sulfuric acid. When phenolphthalein and phosphorus pentoxide are mixed in a mortar a pink color first appears. Gradually the color changes to brown. If exposed to the atmosphere for a longer time the mixture is converted into a dark brown, sticky mass. Finally it becomes practically colorless leaving a precipitate of phenolphthalein. If the experiment is carried on in the absence of moisture the color change is very slow, many days being necessary before a color change is apparent. This shows that the presence of water facilitates the reaction up to a certain point. Then an excess decomposes the resulting compound. This can be explained by the fact that at first the water attacks the phosphorus pentoxide forming metaphosphoric acid, according to the equation:



The metaphosphoric acid combines with the phenolphthalein as in the case of the sulfuric acid, forming a colored oxonium salt according to this equation:

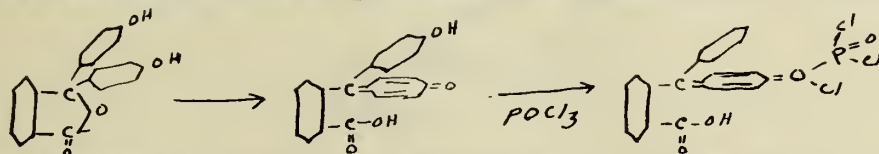


This reaction continues until all the phosphorus pentoxide has been converted into metaphosphoric acid. On further exposure the moisture attacks the colored compound, causing hydrolysis, first going to the carbinol, then to the lactone,



Reaction with phosphorus oxychloride.

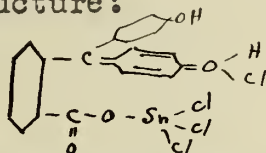
The next reaction studied was phosphorus oxychloride and phenolphthalein. By gently heating phosphorus oxychloride and phenolphthalein, a dark red solution is obtained. On pouring this dark red solution into ice water, a flocculent orange precipitate is obtained. This precipitate was filtered and washed with ice-water until the wash waters gave no test for phosphorus or chlorine. The precipitate was hurriedly dried by pressing between filter paper. Rapid drying was necessary since the compound seemed to hydrolyze very easily. When dry, the powdered substance has a reddish orange color. A sodium fusion showed the presence of chlorine and phosphorus. An attempt was made to analyze this compound, but it was not pure. The results obtained in the analysis were not satisfactory, although it retains most of its color and is not as easily hydrolyzed after it is dry. This compound is more stable than the sulfate or phosphate. This reaction presumably takes place as follows:



The degree of stability depends upon the fact that the chlorine is linked to the oxygen in this compound, whereas the hydroxyl group is linked to the oxygen in the case of sulfuric acid; the chlorine being less easily split off than the hydroxyl.

Reaction with anhydrous metallic salts.

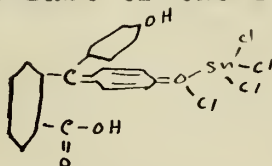
The behavior of phenolphthalein with anhydrous metallic salts like aluminium chloride, stannic chloride, and zinc chloride was first investigated by Meyer and Hantzsch(17). They concluded that phenolphthalein formed oxonium salts which they accorded the following structure:



These compounds are highly colored double salts according to their conclusions.

In the present investigation the author does not agree with the formation as shown by Meyer and Hantzsch, but concludes that these salts react similarly to the sulfate.

The aluminium and tin salts were prepared according to Meyer and Hantzsch. These salts are unstable and hydrolyze very easily, similar to the sulfate. In studying the reaction, the author concludes that an oxonium salt of the following structure is formed:



Meyer and Hantzsch have found that a colored hydrochloride exists at 30°C., which has oxonium structure ($R \text{---} \text{C}^+ \text{---} \text{O} \text{---} \text{Cl}^-$).

The fact that the hydrochloride does not exist at ordinary temperatures and the tin salt does, leads to the conclusion that the hydrochloride is not linked to the oxygen as shown in the tin salt by Meyer and Hantzsch. The author believes that the stannic chloride combines to the oxygen, leaving the carboxyl

group intact. K. Meyer(18) has shown that quinones combine with stannic chloride to give highly colored oxonium salts. This further substantiates the theory that the stannic chloride goes on the oxygen of the quinone group in phenolphthalein. The quinone salts are hydrolyzed very readily, as in the case of phenolphthalein.

Summary

1. Phenolphthalein forms colored substances with certain anhydrous acidic substances, such as concentrated sulphuric acid, phosphorus pentoxide, phosphorus oxychloride; and with anhydrous metallic salts like aluminium chloride, stannic chloride and zinc chloride.

2. These colored substances have not been isolated, because they are either insoluble in the various solvents tried, or are decomposed by them.

3. The colors are explained by the presence of the quinoid group.

4. It is assumed that the quinoid nucleus forms oxonium salts with the above reagents, analogous to the oxonium salts of benzoquinone.

5. In the equilibrium of the various forms of phenolphthalein,

Lactone form \rightleftharpoons Quinoid Form \rightleftharpoons Oxonium salt,

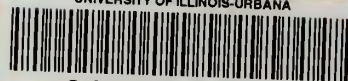
acid dehydrating agents tend to shift the equilibrium towards oxonium salt formation; water in the reverse direction.

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